**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Derivation of the stoichiometric coefficient of water (ν_w) to account for water uptake by atmospheric aerosols" *by* S. Metzger et al.

Anonymous Referee #2

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I agree with the detailed criticisms of Lescroart. In my opinion the derivation is based on half understood borrowings from the solution chemistry literature, and the derivation itself results in dimensionally incorrect and seemingly nonsensical equations like (10f) which relates a stoichiometric coefficient of water (supposed to account for still inadequately explained effects of what the authors term "hydration") to the base-10 logarithm of the mass fraction of solute.

I had expected, after the many criticisms of the supposedly thermodynamic elements of their previous papers, that the authors would take great care to relate their work to established theory, and particularly to the Gibbs-Duhem equations and the known

relationship between water activities and solute activity coefficients. Within the same model, the two should be consistent. However, the authors make no attempt to do this and it is hard to avoid the conclusion that they simply do not understand what they are doing.

Regarding activity coefficients: the authors claim (as they have done before) they are not needed for solid/liquid equilibrium. Of course this is not true - they are required for accurate predictions of any equilibrium that involves solute species, unless the solution is ideal (not the case here). The reason the authors make this statement, as far as I can tell, is that their derivation of the terms that go into the calculation of RH/concentration relationships are based upon the properties of a saturated solution. (So the RH is right for a saturated solution, at least for single solutes).

However, gas/liquid equilibrium in the atmosphere involves aqueous aerosols of all concentrations and the authors introduce the bizarre eq A12 with relates solute activity coefficients to water and solid solute density. I'll state the obvious here: this equation can't possibly be thermodynamically consistent with the expression for solution concentration as f(RH). The only relationship between activity coefficients and solution densities that I am aware of is via the differential of the Gibbs energy (which relates molar volumes in solution to the differentials of the activity and osmotic coefficients with respect to pressure). This relationship has nothing to do with what the authors propose.

And how do the expressions work out in practice? The striking thing about the authors' figure of water uptake vs RH is that their equation becomes less accurate as 100 % RH (pure water) is approached - the opposite of what one would expect. Calculated osmotic coeffients of NaCl, from the authors' expression, are about right at saturation for the reasons given above, but then fall as the solution is diluted (to about 0.17 at 0.02 mol kg-1 NaCl) and do not rise to unity at infinite dilution as they should. This behaviour is very inaccurate, does not correspond to the well-measured and well-undertood behaviour of electrolyte solutes, and is greatly inferior to established models. However, it

is not unexpected given that the authors' model is both misconceived and in any case flawed in its derivation, as established in the numerous criticisms in both Lescroart's review and by reviewers of previous ACP submissions by Metzger et al.

In successive manuscripts the authors simply repeat themselves, do not meet referees' objections, and fail to be clear in most of their explanations. Where they are clear they seem to be wrong. I cannot support the publication of this work. I strongly recommend rejection.

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